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METHOD FOR MANUFACTURING ZIRCONIUM ALLOYS AND ALLOYS MANUFACTURED ACCORDING TO THE METHOD

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ABSTRACT OF THE DISCLOSURE

In making a zirconium alloy of the known type, which, besides zirconium and an insignificant amount of impurities, essentially contains only 0.2–2.5 wt. percent tin and in total 0.1–3.0 wt. percent of one or more of the elements iron, chromium, nickel and niobium and which at higher temperatures have β -phase structure and at lower temperatures have α -phase structure, the inventive object is to give the alloy such an α -phase structure that when the β -phase is transformed to α -phase, a raised ductility and improved surface properties are obtained. This object is met by including, amongst the components when the alloy is manufactured by melting, one or more metallic carbides the metallic carbide so added being in such an amount that the final carbon content of the alloy is 140–300 parts of weight per million parts of weight of the alloy.

The present invention relates to a method of making zirconium alloys of the known type which essentially contain, besides zirconium and an insignificant amount of impurities, from about 0.2 to about 2.5 weight percent tin and in toto from 0.1 to 3.0 weight percent of one or more of the elements iron, chromium, nickel and niobium, whereby to give the alloys a higher than conventional ductility and improved surface properties.

Alloys of this kind, known as "Zircaloy 2" and "Zircaloy 4" respectively, which besides tin contain small quantities of iron, chromium and nickel, or iron and chromium, respectively, have been found especially suitable for use in canning tubes ("tubes de gaine") for atomic reactors because of their good strength, and also their corrosion resistance at higher temperatures, and their small cross-section for absorption of neutrons.

In cooling such an alloy from a high temperature, for instance from 1000° C., there occurs a transformation from a high-temperature phase β (beta) (cubic body-centered lattice) to a low-temperature phase α (alpha) (hexagonal close-packed lattice). During the transformation there are formed platelets (discs) of α -phase from nuclei in the β -crystals, which platelets then grow along specific crystal planes in the β -crystals, i.e., so-called "habit planes." The type of transformation is per se well known and is called "Widmanstätten-transformation."

As a rule, the transformation occurs in such a way that each β -crystal is penetrated by groups of substantially parallel discs of α -phase. It is probable that the points of nucleation for the α -phase discs in the main have been situated in the grain boundaries of the β -crystals, which circumstance has resulted in that adjacent nuclei in such a grain boundary have had very similar conditions for their formation, resulting in a growth of similarly orientated discs. The structure thus formed is, in the following, called "A-structure."

It has now been found that formation of nuclei can be caused within the β -crystals. The points of nucleation are

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then situated adjacent to particles in the crystals. At each such particle the nuclei of several α -phase discs are formed, which discs then grow in different directions. Discs which have grown from different nucleating particles will cross each other, resulting in that the structure looks like a plaited network, often referred to as "basket weave structure." This structure is, in the following, called "B-structure."

The B-structure is, in several respects, more advantageous than the earlier mentioned A-structure, i.e. with regard to the ductility and surface property of the material.

As an example of how the surface properties depend on the structure it can be mentioned that in the manufacture of canning tubes heat-treatment is, as a rule, performed in the β -phase range, so that the transformation to A-structure will be based on relatively coarse β -phase crystals. Because of the great units of uniformly orientated α -phase plates which then are formed, as well as the mechanical anisotropy of the α -phase per se, the flow of material in a subsequent plastic treatment becomes irregular, which condition causes irregular surfaces resulting in a lessened yield. If, however, a B-structure is obtained, the surfaces become smooth.

As mentioned above, the B-structure is superior to the A-structure with regard to ductility. For instance, in the manufacture of fuel elements when fuel rods, clad with the aforesaid alloy, are joined together by brazing, a portion of the canning tube adjacent the brazing joint undergoes the phase transformation α - β - α . If the transformation β - α gives A-structure, the ductility becomes substantially reduced in comparison with a situation in which the transformation gives B-structure.

Accordingly, for zirconium alloys of the above type it is important that the transformation of β -phase to α -phase leads to the B-structure.

By comprehensive experiments we have found that the desired B-structure can be obtained in the said phase transformation by adding a suitable amount of a metallic carbide when melting together the components of the alloy. The relative amount of the added metallic carbide should be carefully controlled, so that the final alloy has a final carbon content of at least 140, and preferably 150, and at the most 300 parts by weight per million parts by weight of the alloy (140–300 p.p.m.). The addition may normally consist of zirconium carbide, but it is possible to replace the zirconium carbide partially or totally by one or more metallic carbides such as iron, chromium and niobium carbides.

As a rule, the addition of zirconium carbide and/or other metallic carbide ought to be of such a size order that the final carbon content of the alloy does not exceed 400 and preferably amounts to 140–300 parts by weight per million parts by weight of the eventually alloy. If the carbon content is below the aforesaid lower limit, 140 p.p.m., the desired B-structure is not obtained. If, on the other hand, the upper limit 300 is exceeded, the corrosion resistance is impaired. Moreover, it has been found that the metallic carbide addition preferably should be in the form of a powder in order to obtain the favorable result according to the invention.

Because zirconium easily forms oxides and absorbs atmospheric and other impurities at raised temperatures, the constituents of the alloy should be melted in vacuum in an arc furnace. The melting is as a rule started with zirconium sponge and zirconium scrap, desired quantities of the other alloying elements being added. According to the invention it is necessary that said zirconium constituents in total per million parts by weight do not contain more carbon than 100 parts and preferably not more than 75 parts by weight. According to the invention there is

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also added zirconium carbide, and/or other metal carbides, in such a quantity that the final alloy obtains the carbon content earlier referred to. The raw materials shall be as pure as possible but often it cannot be avoided that insignificant amounts of impurities, among them carbon, may occur therein. According to the invention it is essential that these impurities be held to a low amount, and that at least 50%, and preferably at least 80%, of the carbon of the final alloy be carbon which has been supplied by the additions of zirconium carbide and/or other metal carbides. In this connection, it can be mentioned that in certain cases insignificant amounts of oxygen and/or silicon may be present in the alloy as an active constituent.

The invention will now be illustrated by an example relating to the manufacture of "Zircaloy 2," containing in percent by weight 1.4% tin, 0.12% iron, 0.10% chromium, 0.06% nickel and the remainder zirconium with insignificant amounts of impurities.

The initial materials for the melting, which was performed in an arc furnace under vacuum, were zirconium sponge, zirconium scrap and desired minor quantities of the other alloy constituents. The carbon content in the initial material was about 0.005 percent of weight. To the above-mentioned initial material there was added 0.15 percent of weight of zirconium carbide.

A comparison of the structure between the material manufactured according to the invention (I) and a corresponding material (II) manufactured from a normal initial material in conventional manner resulted for I in a uniform B-structure and for II in a uniform A-structure after a heat treatment in the β -range as in brazing. In a special tension test on a material thus treated a strain of 13% was obtained for material I and 6% for material II. After heat treatment in the β -range material in a smooth surface resulted, while material II had an irregular and rough surface.

According to a further example "Zircaloy 4," containing in percent by weight 1.5% tin, 0.21% iron, 0.12% chromium and the remainder zirconium with insignificant amount of impurities was produced by melting in an arc furnace under vacuum a material which except for an addition of 0.12% by weight of chromium carbide was practically free from carbon. After hot working in the β -range the alloy had a smooth surface, while an alloy of the above kind produced in a conventional way had an irregular and rough surface.

In each of these exemplary alloy products the final carbon content was between 150 and 300 parts by weight per million parts by weight of the total alloy.

We claim:

1. A method of manufacturing a zirconium alloy containing, besides zirconium and an insignificant amount of

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impurity, 0.2–2.5% by weight of tin and a total amount of 0.1–3.0% by weight of one or more of the elements iron, chromium, nickel and niobium, and an amount of carbon as hereinafter defined, the zirconium alloy having a β -phase structure at higher temperatures and an α -phase structure at lower temperatures, comprising melting one or more zirconium components having in total per million parts by weight a carbon content not exceeding 100 parts by weight and adding thereto one or more metallic carbides together with the further components corresponding to the composition of the alloy required, whereby the metallic carbide or carbides are added in an amount such that the final carbon content of the zirconium alloy is 140–300 parts by weight per million parts by weight of the zirconium alloy.

2. Method according to claim 1, wherein the final carbon content of the zirconium alloy exceeds 150 parts by weight per million parts by weight of the zirconium alloy.

3. Method according to claim 1, wherein the metallic carbide is added in the form of a powder.

4. Method according to claim 1, wherein the added metallic carbide is zirconium carbide.

5. Method according to claim 1, wherein the metallic carbide is added in an amount such that the final carbon content of the zirconium alloy is 170–300 parts by weight per million parts by weight of the zirconium alloy.

6. Method according to claim 1, wherein at least 50% by weight of the carbon in the final alloy is supplied by the addition of metallic carbide.

7. Method according to claim 6, wherein at least 80% by weight of the carbon in the alloy is supplied by the addition of metallic carbide.

8. Method according to claim 1, wherein the zirconium alloy is manufactured by melting in vacuum in an arc furnace.

9. A zirconium alloy when manufactured by the method defined in claim 1.

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